

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>C08F 8/30</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/13142</b>  <b>(43) International Publication Date:</b> <b>8 July 1993 (08.07.93)</b>
<b>(21) International Application Number:</b> PCT/US92/10315 <b>(22) International Filing Date:</b> 30 November 1992 (30.11.92)  <b>(30) Priority data:</b> 07/814,656 30 December 1991 (30.12.91) US  <b>(71) Applicant:</b> PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US).  <b>(72) Inventors:</b> SWARUP, Shanti ; 5184 Carterton Drive, Gibsonia, PA 15044 (US). SUNDARARAMAN, Padmanabhan ; 1917 Red Coach Road, Allison Park, PA 15101 (US). MCCOLLUM, Gregory, J. ; 5130 Bronwyn Court, Gibsonia, PA 15044 (US). KANIA, Charles, M. ; 1024 Woodland Place, Natrona Heights, PA 15065 (US). CLAAR, James, A. ; 201 Heston Drive, Mars, PA 16046 (US).		<b>(74) Agents:</b> PINGITORE, L. ; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.  <b>(81) Designated States:</b> AU, BR, CA, FI, JP, KR, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> AZETIDINOL REACTION PRODUCTS  <b>(57) Abstract</b>  An ungelled reaction product is prepared from a carboxylic acid group containing polymeric material and an azetidinol containing material having one azetidinol moiety per molecule. The ungelled reaction product is particularly useful as a grind vehicle for pigment grind compositions.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

- 1 -

## AZETIDINOL REACTION PRODUCTS

Cross Reference to Related Applications

5           This application is related to U.S. Patent Application Serial  
Number \_\_\_\_\_, filed \_\_\_\_\_, entitled \_\_\_\_\_.

Background of the Invention

10           The present invention relates to azetidinol containing  
materials having one azetidinol moiety per molecule and reaction  
products prepared therefrom.

          Acrylic polymers have been well known as vehicles for  
coating compositions as well as for pigment grind pastes used in  
formulating such coating compositions. They can provide tough,  
15 resilient and durable coatings with excellent aesthetic properties.

          Small nitrogen ring containing materials such as aziridines  
have been used as modifiers for coating compositions such as those  
described above for sometime. For example, U.S. 3,290,417 to  
Christenson et al discloses that the overall properties of coatings  
20 based on interpolymers of hydroxyalkyl esters are greatly improved by  
the inclusion of a small proportion of acidic units in the polymeric  
vehicle and reacting these acidic groups with an alkyleneimine or a  
substituted alkyleneimine. A further example is U.S. 3,290,416 which  
discloses coating compositions containing polymerized alkyl  
25 methacrylates which have been modified to improve their properties by  
the inclusion of imine-reacted acidic groups.

          Aziridines, however, despite their potential for improving  
the overall properties of coatings formulated with the polymers they  
modify, are highly reactive materials which have a number of  
30 attendant disadvantages. Their highly reactive nature makes them  
unstable and in addition they are highly toxic requiring special  
conditions for handling. The most commonly available forms, ethylene  
imine and propylene imine are low molecular weight materials which are  
so unstable, safe transportation is virtually impossible. Moreover  
35 they are highly toxic materials which may have carcinogenic side  
effects.

- 2 -

In addition, materials derived by reacting ethylene imine or propylene imine with carboxylic acids tend to undergo rearrangement to the corresponding amide under certain severe conditions like prolonged heating thereby reducing the yield of desired aminoester product. Further, their high reactivity often results in a small amount of homopolymer by-product formation. The homopolymer causes the final film to be hazy thus impairing the appearance properties of coatings prepared from these materials.

There is a need for a way to prepare modified acrylic polymers which have all of the beneficial properties of the aziridine modified materials but without the attendant disadvantages.

#### Summary of the Invention

In accordance with the present invention there is provided an ungelled reaction product of a carboxylic acid group containing polymeric material and an azetidinol containing material having one azetidinol moiety per molecule.

#### Detailed Description of the Invention

Azetidinol containing materials having one azetidinol moiety per molecule are very useful as providers of aminoester groups for modifying acrylic polymers and a variety of other oligomers and polymers without the handling hazards attendant to aziridines. Contrary to what has been theorized by some skilled artisans, for example U.S. 3,705,076 assigned to E.I. du Pont de Nemours, column 6, lines 48 to 53, azetidines are not as reactive as the 1,2 imines, thus the azetidines present small danger in handling.

Oligomers and polymers such as acrylics modified with azetidinol containing materials having one azetidinol moiety per molecule can be prepared at low cost in high yield from readily available raw materials under ordinary processing conditions without significant concern for toxic side effects or safety hazards. The stability of the such azetidinol materials also results in better stability upon shipping and storage and improved film properties when

- 3 -

the materials are used in coating applications. The azetidins do not undergo rearrangement or homopolymerization as readily as the aziridines mentioned above in the background.

The ungelled reaction products of the present invention which are prepared from azetidinol containing materials having one azetidinol moiety per molecule, therefore, are very advantageous in coating applications. When prepared from acrylic polymers, the ungelled reaction products are most useful as pigment grind vehicles. They are also useful for general coating applications.

10 The claimed ungelled reaction products, as was mentioned above, have as one reactant, a carboxylic acid group containing polymeric material. The carboxylic acid group containing polymeric material can be selected from a variety of materials. Examples of suitable materials include vinyl addition polymers prepared from the

15 vinyl addition polymerization of vinyl monomers, polyesters, polyethers, polyurethanes and polyamides. A detailed description of all of these materials is not felt to be necessary since one skilled in the art of coatings enjoys extensive knowledge of these materials. If additional information is desired see Kirk Othmer, Encyclopedia of

20 Polymer Science and Technology, John Wiley and Sons, Inc. Copyright 1964. The carboxylic acid group containing polymeric material generally has an acid value of at least 2.5, preferably at least 5. Generally the acid value ranges from about 5 to about 130.

The acid value is the number of milligrams of potassium

25 hydroxide required to neutralize the free acids present in one gram of polymer sample. The determination is made by titrating the sample in a suitable solvent such as ethanol or acetone using phenolphthalein or phenol red as indicator.

A preferred carboxylic acid group containing polymeric

30 material is a carboxylic acid functional acrylic polymer. This preferred polymer will be discussed in detail below.

The aforesaid acrylic polymer can be prepared by the vinyl addition polymerization of a vinyl monomer component which comprises at least a portion of a carboxyl functional vinyl monomer. Examples

35 of suitable carboxyl functional vinyl monomers include acrylic acid,

BEST AVAILABLE COPY

- 4 -

methacrylic acid, monoesters of unsaturated dicarboxylic acids such as maleic acid, fumaric acid, and itaconic acid, for example, mono(hydroxyethyl) and mono(hydroxypropyl) esters of maleic acid.

The balance of the vinyl monomer component can include a variety of other vinyl monomers which contain polymerizable vinyl unsaturation. For example, hydroxyl functional vinyl monomer such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate and 2-hydroxybutyl methacrylate. Also useful are acrylamide; N-methylolacrylamide and N-alkoxymethyl acrylamides such as N-ethoxymethyl acrylamide and N-butoxymethylacrylamide; tertiary-butylaminoethyl methacrylate; sulfoethyl methacrylate; and alkyl acrylates and methacrylates which contain from 1 to 18 carbon atoms in the alkyl portion such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isodecyl (meth)acrylate and isobornyl (meth)acrylate. Also useful are styrene, para-methyl styrene, alpha-methyl styrene, acrylonitrile, methacrylonitrile and vinyl esters such as vinyl acetate or vinyl versatate. Mixtures of the aforesaid monomers can also be utilized. Preferably, the acrylic polymer has a number average molecular weight ranging from about 500 to about 50,000, more preferably about 2000 to about 20,000.

To obtain the advantages of the present invention, the amount of carboxyl functional vinyl monomer in the vinyl monomer component generally ranges from about 0.1 percent by weight to about 35 percent by weight or more, the percentages based on the total weight of the vinyl monomer component. When the ungelled reaction product is used as a grind vehicle the amount of carboxyl functional vinyl monomer in the vinyl monomer component preferably ranges from about 0.5 percent by weight to about 5 percent by weight. When the ungelled reaction product is used as a film former in coating compositions, the amount of carboxyl functional vinyl monomer in the vinyl monomer component preferably ranges from about 1 percent to about 20 percent by weight.

- 5 -

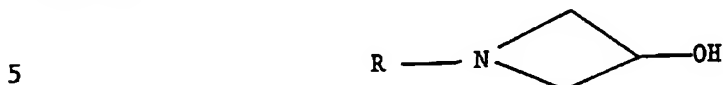
Preparation of the vinyl addition polymer is usually conducted at a temperature within the range of about 25°C to about 250°C, preferably 85°C to 160°C. There is generally present a free radical initiator which is selected from a wide variety of materials. Suitable types of materials include peroxides, hydroperoxides and azo initiators. Examples of these types of initiators include di-tertiary butyl peroxide, di-cumyl peroxide; amyl peroxyacetate; cumene hydroperoxide; 2,5-dimethyl-2,5-bis(tertiary butyl peroxy)hexane; hexyne-3-tertiary butyl cumyl peroxide; tertiary amyl peroxide; 2,5-dihydroperoxy 2,5-dimethylhexane; di(n-propyl)peroxydicarbonate and 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile). Also suitable are Redox initiators such as the combination of hydrogen peroxide and isoascorbic acid. Transition metals such as iron are usually used as cointiators with a redox initiator system in aqueous polymerization.

The type and amount of initiator will be selected depending upon the molecular weight desired and/or the final form of the polymeric species, i.e., solvent soluble form or dispersed form in aqueous or non-aqueous media. The amount of initiator can vary widely although usually it is present in an amount ranging from about 0.1 percent to about 8 percent, the percentage based on the total weight of the vinyl monomer component. Generally, there may also be present during the vinyl addition polymerization a solvent which also may assist in maintaining the preferred reaction temperature. Examples of these solvents include ketones such as methyl amyl ketone, aromatic petroleum distillates, esters such as butyl acetate, heptyl acetate and 2-ethylhexyl acetate, and high boiling ester solvents such as those commercially available from Exxon Chemical Corporation under the trademark designations EXTATE 600 and EXTATE 700.

It should be understood that the carboxylic acid functional acrylic polymers may also be prepared by conventional suspension, emulsion and non-aqueous dispersion polymerization techniques.

- 6 -

The azetidinol containing material having one azetidinol moiety per molecule can be represented by the following structural formula:



wherein R is C<sub>1</sub> to C<sub>20</sub> alkyl, C<sub>3</sub> to C<sub>7</sub> cycloalkyl or aralkyl. Examples of suitable alkyl groups include methyl, isopropyl, tertiary butyl and octyl. Examples of suitable cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. A representative aralkyl group is benzyl. Preferably, R is cyclohexyl. These products are most suitable as pigment grind vehicles.

R can also be an oligomeric or polymeric moiety such as for example an alkoxy terminated polyether. These products are most suitable as film forming vehicles for coating compositions.

The azetidinol containing materials having one azetidinol moiety per molecule generally can be prepared by the reaction of an amine with epihalohydrin followed by removal of hydrogen halide. The reaction is preferably conducted in the presence of a blend of at least one polar solvent and at least one non-polar solvent. The polar solvent is a dipolar aprotic solvent having a dielectric constant at 25°C of at least 30.

Suitable amine containing materials include primary amines such as butylamine, hexylamine, hydroxy propylamine, tertiary butylamine and cyclohexylamine. Suitable epihalohydrins include epichlorohydrin and epibromohydrin. Examples of polar solvents include acetonitrile, methanol, ethanol, isopropanol, butanol, dimethylformamide and dimethylsulfoxide. Examples of non polar solvents include toluene, xylene and heptane.

Preferably, the amine containing material is cyclohexylamine, the epihalohydrin is epichlorohydrin, the polar solvent is acetonitrile and the non polar solvent is toluene.



- 7 -

After the initial mixing, the cyclohexylamine and epichlorohydrin are reacted at a temperature and for a period sufficient to form the hydrochloride salt of the N-cyclohexyl azetidinol. Generally, the reaction temperature ranges from about 5 70°C to about 80°C and the time ranges from about 1 to about 6 hours.

In a preferred embodiment of the invention, the hydrochloride salt of the N-cyclohexyl azetidinol is converted to the free amine base by neutralization with aqueous sodium hydroxide.

Preferably, after converting the hydrochloride salt of the 10 N-cyclohexyl azetidinol to the free amine base, the product can be optionally stripped to remove water and the salt removed by filtration to yield a solution of the N-cyclohexyl azetidinol. Crystalline N-cyclohexyl azetidinol can be isolated by solvent stripping and recrystallization.

15 In the preferred embodiment detailed above, conversion of the hydrochloride salt of the N-cyclohexyl azetidinol to the free amine base preferably involves the steps of:

- (1) removing up to 70 percent of the polar solvent,
- (2) neutralizing the N-cyclohexyl azetidinol hydrochloride while 20 adding additional non-polar solvent,
- (3) removing a portion of the non-polar solvent, and
- (4) removing the salt by filtration.

The ungelled reaction product of the present invention is prepared by reacting the carboxylic acid group containing polymeric 25 material and the azetidinol containing material to form a covalent bond. The acid groups of the acid functional resin can be fully or partially reacted with N-cyclohexyl azetidinol in such solvents as toluene, xylene or butyl acetate. The temperature of the reaction generally ranges from about 110°C to about 130°C. The progress of 30 the reaction can be monitored by measuring acid value which decreases as acid groups react with azetidinol and becomes constant when all the azetidinol groups are consumed.

The ungelled reaction product is especially suitable as a grind vehicle in preparing pigment grind compositions. It has been 35 observed that the ungelled reaction products enhance color

- 8 -

development of a pigment in a grind paste. Color development is a measure of the color intensity developed in a pigment grind paste relative to a standard.

The grind vehicles of the present invention can be used to grind pigments in a conventional manner well known to those skilled in the art. Typically, a solvent mixture, grind resin, and required amount of pigment are mixed together with a cowles blade for about 15 to about 30 minutes. The resulting paste is then passed through an Eiger Mill operating at 4000-6000 rpm. until a Hegman reading of 7.0 is obtained. Cold water is circulated around the mixing chamber during the operation of the mill to keep the temperature below 40°C. The grind paste, thus obtained, is used to make final paint.

In one particularly preferred embodiment, the ungelled reaction product detailed above is modified by reaction with a triisocyanate and tetraethylene pentamine. This modified ungelled reaction product is especially suitable as a grind vehicle for red pigments.

The ungelled reaction product of the present invention is also suitable as a film former in preparing thermosetting or curable coating compositions for a variety of applications.

The ungelled reaction product of the claimed invention contains an active hydrogen functional material, i.e., a hydroxy aminoalkyl ester, and is capable of being cured with crosslinking agents such as aminoplasts, phenoplasts or blocked polyisocyanates through reaction of the hydroxyl groups.

Polyisocyanates which may be used as curing agents include aliphatic or alicyclic polyisocyanates such as hexamethylene diisocyanate and dicyclohexylmethane diisocyanate; aromatic polyisocyanates such as 2,4- and 2,6-toluene diisocyanate and mixtures thereof, and diphenylmethane-4,4'-diisocyanate; arylalkyl polyisocyanates such as ortho-, meta- and para-xylylene diisocyanate; isophorone diisocyanate; polyurethane polyisocyanates obtained from reacting polyisocyanates such as those mentioned above with polyhydroxy compounds such as ethylene glycol and trimethylolpropane. Polyisocyanates containing isocyanurate, allophanate or biuret groups can be also used.

- 9 -

When polyisocyanates are used as curing agents in compositions containing polymer products of the invention, an effective amount of a catalyst for promoting cure between hydroxyl groups of the polymer product and isocyanato groups of the polyisocyanate may be incorporated. Examples of such catalysts include tertiary amines such as triethylamine or 1,4-diazobicyclo-(2:2:2)octane, and organotin compounds such as stannous octoate and dibutyltin dilaurate.

The polyisocyanates above can be blocked with a suitable blocking agent which would unblock at elevated temperature, thereby facilitating formulation of a stable one package composition. Examples of blocking agents include lower aliphatic alcohols such as methanol, oximes such as methyl ethyl ketone oxime and lactams such as caprolactam.

Other curing agents which are reactive with active hydrogens in polymer products of the invention include aminoplast resins which are aldehyde condensation products of amines or amides with aldehydes. Examples of suitable amines or amides are melamine, benzoguanamine, urea and similar compounds. Generally, the aldehyde employed is formaldehyde, although products can be made from other aldehydes such as acetaldehyde and furfuryl. Condensation products contain methylol groups or similar alkylol groups depending upon the particular aldehyde employed. If desired, these methylol groups can be etherified by reaction with an alcohol. Various alcohols are employed and generally include any monohydric alcohol, although the preferred alcohol contains from 1 to 4 carbon atoms such as methanol, ethanol, isopropanol and n-butanol. Aminoplasts are commercially available from the American Cyanamid Company under the trademark CYMEL and from the Monsanto Chemical Company under the trademark RESIMINE.

Such curable (crosslinkable) or thermosetting compositions can be formulated as clear coats or optionally they can contain a pigment. The pigments may be any of the conventional types comprising, for example, iron oxides, lead oxides, strontium chromate, carbon black, coal dust, titanium dioxide, talc, barium

- 10 -

sulfate, as well as the color pigments such as cadmium yellow, cadmium red, chromium yellow, phthalocyanine blue, toluidine red, and the metallic pigments such as aluminum flake and metal oxide encapsulated mica. When used, the pigment content of the coating composition is expressed as a pigment to resin weight ratio, and is usually within the range of about 0.05 to 3.0:1.

In addition, other optional ingredients such as adjuvant hydroxy-containing polymers, fillers, plasticizers, catalysts, reactive diluents, anti-oxidants, ultraviolet light absorbers, flow control agents, and other formulating additives can be employed if desired.

Coating compositions of the invention can be applied to a variety of substrates such as wood, metal, glass, cloth, plastic, foams and the like by a variety of application techniques such as air spraying, airless spraying, dipping, brushing and flow coating. The coating compositions are suitable as basecoats or clearcoats and are particularly desirable as topcoat compositions for automobiles and trucks either as original finishes or as refinish coatings. Also, the coating compositions can be applied as color plus clear in basecoat-clearcoat applications.

The following examples are illustrative of the invention and are not intended to be limiting.

- 11 -

Example ISynthesis of N-Cyclohexyl Azetidinol

5 Charge	<u>Parts by Weight (grams)</u>	
Cyclohexyl amine		1244
Toluene		1200
Acetonitrile		3000
10	Feed A Epichlorohydrin	1154
	Feed B Toluene	3400
	Feed C 50% aqueous sodium hydroxide	1030
	Feed D Toluene	2398
15		

Feed A was added over one half hour into the charge at room temperature. The contents in the flask were heated slowly to about 75°C and held for 5 hours at this temperature. The solvents were removed by distillation, followed by addition of Feed B. The flask was cooled to room temperature and Feed C was added. The mixture was agitated for about 40 minutes, filtered to remove the salt and then the solvents were removed by vacuum distillation. Finally Feed D was added. The resulting product was identified by Gas Chromatography and possessed the physical properties which are summarized in Table 1.

Table ICyclohexyl Azetidinol Properties

30	Total Solids (110°C for one hour)	50 percent (toluene)
	Color	Yellow to Brown
	Melting point after purification in 1 part methanol:2 parts ethyl ether	78°C to 80°C
35	Hydroxyl Value (empirical, titrated in 50 percent toluene)	189
	Hydroxyl Value (theoretical)	182
	Milliequivalents amine (theoretical)	3.2
	Acid Value	3.0 ± 2
40	Molecular Weight (solid material)	154
	Chlorine	0.05 to 0.1 percent
	Water	less than 0.05 percent
	Weight/gallon	7.834 grams
	Molecular Weight by Gel	
45	Permeation Chromatography (GPC)	number average (Mn) 111
		weight average (Mw) 153
		Peak 237

- 12 -

Example IIPreparation of Azetidinol Modified Acrylic A

5     1,209.9 grams of an aliphatic/aromatic hydrocarbon (B.P. Range 110-126°C) was heated to 119°C.

At 119°C two simultaneous additions of monomer and free radical initiator were made over a 3 hour period. The monomer feed comprised 416.05 g hydroxyethyl acrylate, 75.05 g methacrylic acid, 25.0  
10 acrylic acid, 1,248.15 g styrene, 832.1 g 2-ethylhexyl acrylate, 811.3 g butyl methacrylate, 748.9 g methyl methacrylate, and 54.1 g t-dodecyl mercaptan. The initiator feed comprised 422.55 g toluene and 62.4 g t-amyl peroctoate. Upon completion of the two feeds a solvent mix of 151.8 g of the above hydrocarbon and 51.5 g isobutanol  
15 was added to the reaction. An initiator feed comprised of 291.95 g of the hydrocarbon, 96.1 g isobutanol and 20.8 g t-amyl peroctoate was added over a one hour period with the temperature remaining at about 120°C. Upon completion of this feed, 74.8 g of the hydrocarbon and 25.3 g isobutanol were added and the reaction held at about 120°C  
20 for one hour. At this point a mixture of 850.8 g hydrocarbon, 672.15 g isobutanol and 132.65 g cyclohexyl azetidinol (35.5% in Toluene) was added and a temperature of about 105°C was maintained for one more hour.

The product solution had a solids content of 51.7%, a Gardner  
25 Holdt viscosity of 5.7 stokes (T), an acid value of 8.44 and a number average molecular weight of 7322 as determined by Gel Permeation Chromatography, GPC.

Example IIIPreparation of Azetidinol Modified Acrylic B

30     Polymer B was prepared in a manner similar to Polymer A except that after the cyclohexyl azetidinol reaction of one hour was complete, Polymer A was further modified by cooling to 40°C to prepare Polymer B.

- 13 -

16.45 g of tetraethylene pentamine were then added, followed by the addition of a mixture comprises of 126.75 g butyl acetate and 77.1 g DESMODUR N, (isocyanurate of isophorone diisocyanate commercially available from Mobay Chemical Corporation; 80% solids in Dowanol PM Acetate). The reaction was finished upon completion of this feed.

The product solution had a solids content of 52.55%, a Gardner Holdt viscosity of 8.5 stokes (V), an acid value of 8.38, a number average molecular weight of 6183 by GPC. The infrared spectrum showed no free isocyanate.

#### Example IV

##### Preparation of Polymer C

##### Comparative Example

15

Polymer C was prepared in the same manner as Polymer A except that the cyclohexyl azetidinol was omitted.

#### Example V

##### Preparation of Polymer D (alkyleneimine modified)

##### Comparative Example

Polymer D was prepared in the same manner as Polymer A except that the cyclohexyl azetidinol solution was replaced by hydroxyethyl ethyleneimine on molar basis.

#### Example VI

##### Preparation of Polymer E

##### (alkyleneimine/amine/isocyanate modified)

30

##### Comparative Example

Polymer E was prepared in the same manner as Polymer B except that the cyclohexyl azetidinol solution was replaced by hydroxyethyl ethyleneimine on a molar basis.

- 14 -

Example VIIPreparation of Polymer F (propyleneimine modified)

## Comparative Example

- 5 Polymer F was prepared in the same manner as Polymer A in Example II except that cyclohexyl azetidinol was replaced by propyleneimine on a molar basis.

Example VIIIPreparation of Polymer G (propyleneimine modified)

## Comparative Example

- 10 Polymer G was prepared in the same manner as Polymer B of Example III except that cyclohexyl azetidinol was replaced by propyleneimine on a molar basis.

Example IXPreparation of Polymer H (Comparative Example)

- 20 Polymer H was prepared in the same manner as Polymer C in Example III except that cyclohexyl azetidinol was omitted.

Example XCarbon black pigment grind paste

- |    |  |                       |
|----|--|-----------------------|
| 25 | <u>Materials</u>   | <u>Amount (pound)</u> |
|    | Carbon black pigment<br>(from Mobay Chemical Corporation)    | 0.78                  |
| 30 | Grind Resin<br>(Examples II, IV, V, VII)-                    | 3.32                  |
|    | Butyl Acetate  | 1.96                  |
|    | Wax (40% solution in xylene,<br>from ChemCentral Industries) | 0.02                  |



- 15 -

Four pigment grind pastes were prepared by mixing the above materials together in Steel Ball Attritor Mill (Size 1S by Union Process Incorporated/Szeguari System Intermill) for several hours until a Hegman reading of 8.0 was reached. Samples of paste were withdrawn every hour and color development was evaluated qualitatively by visual inspection in the following manner. A small pool of each paste was drawn down on a sheet of polypropylene and baked until dry. The dried pastes were inspected for cloudiness, dirt, clumps of pigment and relative color. The results of the inspection are presented in Table 2. Each paste was rated on a scale of 0-5 for the above features, where 5 was best and 0 was worst.

Table 2

Color development at various time intervals for carbon black pigment.

Grind Resin	<u>1hr</u>	<u>2hr</u>	<u>3hr</u>	<u>4hr</u>	<u>5hr</u>
20 Example V	2	2	3	4	5
Example IV	0	0	0	0	0
Example VII	2	2	4	5	5
Example II	5	5	5	5	5

25

Example XI

In this Example, red pigment (Perylene Red from Mobay Chemical Corporation) was ground in a manner similar to the carbon black in Example X using the grind resins prepared in Examples III, VI, VIII and IX. The results for color development are tabulated in Table 3.

Table 3

Grind Resin	<u>1hr</u>	<u>2hr</u>	<u>4hr</u>	<u>5hr</u>
35 Example III	1	3	4	5
Example VI	2	3	4	5
Example VIII	1	2	3	4
40 Example IX	0	0	1	2

- 16 -

Example XII

This example presents grind paste viscosities of carbon black pigment at 43% total solids as ground in Example X (Table 2, 5 hrs).

The lower the grind paste viscosity the better the pigment grinding. (Pastes of all of these Examples demonstrated good pigment grinding)

		Paste Viscosity (centipoise)
10	<u>Resin</u>	
	Example V	150
	Example IV	300
	Example VII	750
	Example II	100
15		

Example XIII

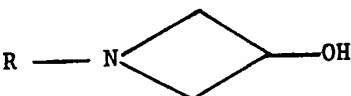
This Example presents grind paste viscosities of perylene red pigment as ground in Example XI (Table 3, 5 hrs) at 43% total solids. The pastes with lower viscosities (Examples III, IX) demonstrated better pigment grinding.

		Paste Viscosity (centipoise)
25	<u>Resin</u>	
	Example III	250
	Example VI	1550
	Example VIII	1900
	Example IX	750

- 17 -

WHAT IS CLAIMED IS:

1. An ungelled reaction product of a carboxylic acid group containing polymeric material and an azetidinol containing material having one azetidinol moiety per molecule.
- 5 2. The ungelled reaction product of claim 1 wherein the carboxylic acid group containing polymeric material is a carboxylic acid functional acrylic polymer.
- 10 3. The ungelled reaction product of claim 2 wherein the carboxylic acid functional acrylic polymer has an acid value of at least 2.5.
4. The ungelled reaction product of claim 3 wherein the acrylic  
15 polymer has a number average molecular weight ranging from about 500 to about 50,000.
5. The ungelled reaction product of claim 1 wherein the azetidinol containing material having one azetidinol moiety per  
20 molecule is represented by the following structural formula:


- wherein R is C<sub>1</sub> to C<sub>20</sub> alkyl, C<sub>3</sub> to C<sub>7</sub> cycloalkyl or aralkyl.
- 25 6. The ungelled reaction product of claim 5 wherein R is cyclohexyl.
7. A pigment grind composition comprising pigment and as a grind  
30 vehicle, an ungelled reaction product of a carboxylic acid group containing polymeric material and an azetidinol containing material having one azetidinol moiety per molecule.
8. The pigment grind composition of claim 7 wherein the ungelled  
35 reaction product has been modified by reaction with a polyisocyanate and polyamine.

- 18 -

9. The pigment grind composition of claim 7 wherein the ungelled reaction product has been modified by reaction with a triisocyanate and tetraethylene pentamine.

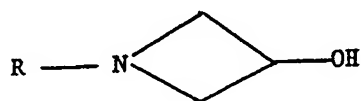
5 10. The pigment grind composition of claim 7 wherein the carboxylic acid group containing polymeric material is a carboxylic acid functional acrylic polymer.

11. The pigment grind composition of claim 10 wherein the  
10 carboxylic acid functional acrylic polymer has an acid value of at least 2.5.

12. The pigment grind composition of claim 9 wherein the acrylic polymer has a number average molecular weight ranging from about 500  
15 to about 50,000.

13. The pigment grind composition of claim 7 wherein the azetidinol containing material is represented by the following structural formula:

20



wherein R is C<sub>1</sub> to C<sub>20</sub> alkyl, C<sub>3</sub> to C<sub>7</sub> cycloalkyl or aralkyl.

25 14. The pigment grind composition of claim 13 wherein R is cyclohexyl.

15. The pigment grind composition of claim 9 wherein the pigment is a red pigment.

30

16. A coating composition comprising, as a film forming vehicle, an ungelled reaction product of a carboxylic acid group containing polymeric material an active hydrogen-containing azetidinol containing material having one azetidinol moiety per molecule; and a  
35 crosslinking agent capable of reacting with the active hydrogens.

- 19 -

17. The coating composition of claim 16 wherein the carboxylic acid group containing material is a carboxylic acid functional acrylic polymer.

5 18. The coating composition of claim 16 wherein the azetidinol containing material is N-cyclohexyl azetidinol.

19. The coating composition of claim 16 wherein the crosslinking agent is selected from aminoplasts, phenoplasts and blocked  
10 polyisocyanates.

20. A method for the preparation of an azetidinol containing material having one azetidinol moiety per molecule which comprises

- 15 (A) admixing an amine containing material and an epihalohydrin in the presence of a blend of at least one polar solvent and at least one non-polar solvent, the polar solvent being a dipolar aprotic solvent having a dielectric constant at 25°C of at least 30; and
- 20 (B) reacting the amine containing material and epihalohydrin at a temperature and for a period sufficient to form the acid salt of an azetidinol containing material having one azetidinol moiety per molecule.

21. The method of claim 20 further comprising step (C) converting  
25 the acid salt of the azetidinol containing material to the free amine base.

22. The method of claim 20 wherein the non-polar solvent is  
toluene.

30

23. The method of claim 20 wherein the polar solvent is acetonitrile.

## INTERNATIONAL SEARCH REPORT

PCT/US 92/10315

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F8/30		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08F ; C09D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	DE,A,1 469 525 (DOW CORNING CORP.) 23 January 1969 see the whole document	1
A	US,A,3 325 443 (R. M. CHRISTENSON) 13 June 1967 see the whole document	1
A	FR,A,2 224 498 (SANDOZ S. A.) 31 October 1974 see claims 1-29	1
A	BE,A,654 889 (MONSANTO) 27 April 1965 see page 27 - page 29	1
A	GB,A,867 398 (ROHM & HAAS) 10 May 1961 see claims 1-12	1
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22 MARCH 1993	14. 05. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	PERMENTIER W.A.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210315  
SA 67949

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-1469525	23-01-69	BE-A- 653978	05-04-65
		FR-A- 1416604	
		GB-A- 1032139	
		NL-A- 6411492	05-04-65
		US-A- 3332797	
		US-A- 3321432	
-----			
US-A-3325443		None	
-----			
FR-A-2224498	31-10-74	CH-A- 596244	15-03-78
		DE-A- 2416022	24-10-74
		GB-A- 1467156	16-03-77
		JP-A- 50052199	09-05-75
		US-A- 3980682	14-09-76
-----			
BE-A-654889	27-04-65	CH-A- 460517	
		DE-A- 1570914	15-10-70
		FR-A- 1423767	
		GB-A- 1088208	
		NL-A- 6412318	29-04-65
		US-A- 3291679	
-----			
GB-A-867398		None	
-----			